

Soft X-ray emission spectroscopy of early-transition-metal compounds

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INTRODUCTION

It is well known that transition metal compounds are very useful materials for applications. Here, the problem is how we could know the information of the electronic structure of early transition metal compounds by measuring the soft x ray Raman scattering. It is known that the transition metal compounds have narrow band dispersions. Instead of the band dispersion curve, we might know the charge transfer energy Δ and the d-d Coulomb interaction energy U , and the other important parameters that decide the electronic structure of transition metal compounds.

It is known that the heavy transition metal compounds belong to the charge transfer insulators, because charge transfer energy is smaller than the Coulomb energy. On the other hand, early transition metal compounds belong to the Mott-Hubbard insulators, because the Coulomb energy is smaller than the charge transfer energy. In the case of late transition metal compounds, the elementary excitation has been already known to be d-d transition within 3d states. It is a problem what is it in the early transition metal compounds.

EXPERIMENTAL

Soft x-ray emission measurements were carried out at BL19B in Photon Factory(PF) at KEK and at BL8 in Advanced Light Source(ALS) at LBNL. The Sc and Ti compounds were measured at PF. The Cr and V compounds were mainly measured at ALS.

RESULTS AND DISCUSSION

Figure 1 shows the comparison between the photoemission¹ and several soft x-ray emission spectra² of vanadium dioxide VO_2 .

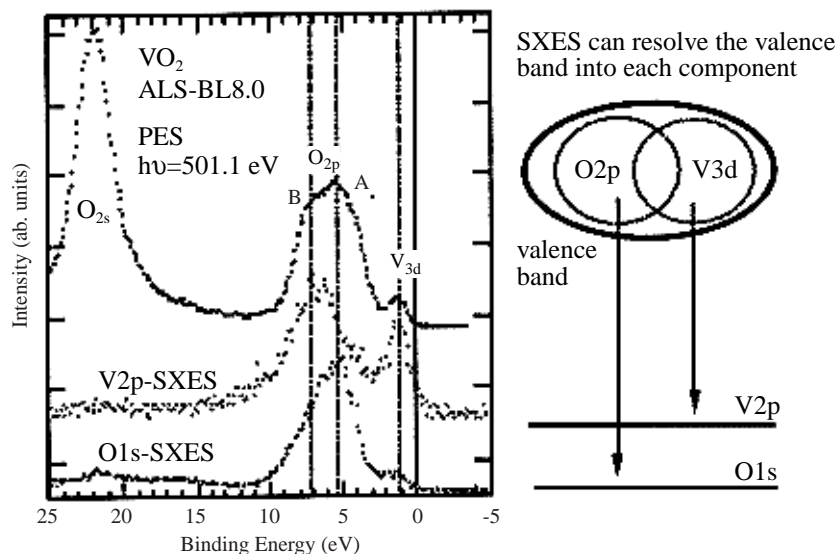


Fig. 1. Comparison of the photoemission spectrum and V L₃-, V L₂-, and O K-SXE spectra of VO_2

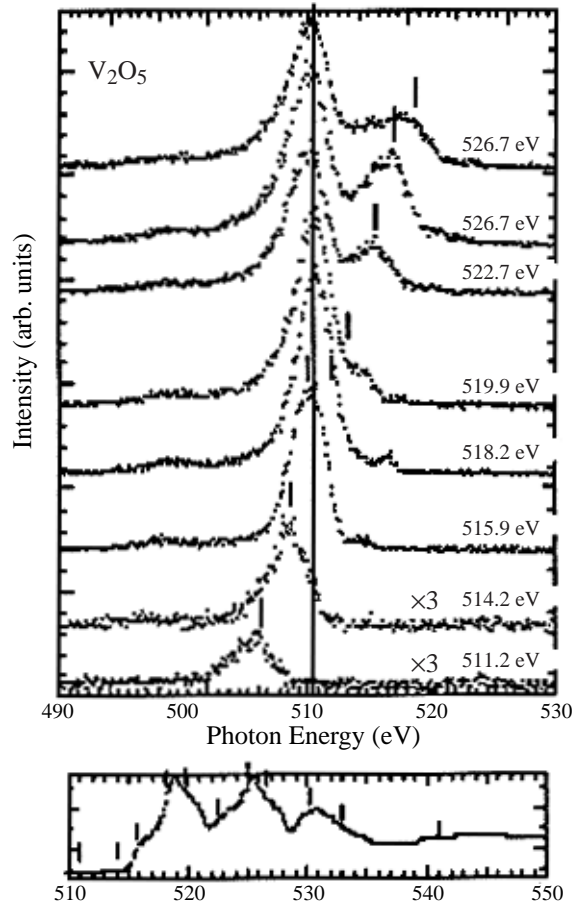


Fig. 2. Upper panel shows the V $L_{2,3}$ -SXE spectra of V_2O_5 measured by various photon energies. The lower panel shows the total electron yield spectrum of V_2O_5 . The vertical bars in the lower panel correspond to the photon energies where the SXE spectra were measured.

band at lower binding energy band and that of the V2p emission spectra coincides with that of the O2p band at the higher binding energy as well as the V3d band at Fermi level. The band B has a strong 3d component in the O2p band. On the other hand, it is also found that there is an intensity of O2p component in the 3d band at Fermi level. These facts show both components are strongly hybridized with each other.

In the case of the nominally d^0 system, there is no d-d transition. Figure 2 shows soft x-ray emission spectra³ of V_2O_5 . One Raman scattering band is found at around 6.2 eV, as indicated by vertical bars. This band is thought to correspond to the transition from the O2p valence band to the V3d conduction band.

The dots in the middle are the V2p emission spectrum and the lowest is the O1s emission spectrum. It is known that the valence band of VO₂ mainly consists of O2p and V3d components. Vanadium 2p emission reflects V3d partial density of state and O1s emission reflects O2p partial density of state. The sum of the two soft x-ray emission spectra roughly equal to the photoemission spectrum, if we consider the cross section of each component. The valence band can be resolved into the V3d and O2p components by soft x-ray emission spectra. It is known that the photoemission spectra have two main bands; the O2p component is dominant at higher binding energy and the V3d component is located just below Fermi level. Furthermore, the O2p bands have two structures. It is found that the energy position of O1s soft x-ray emission spectroscopy coincides with that of the O2p

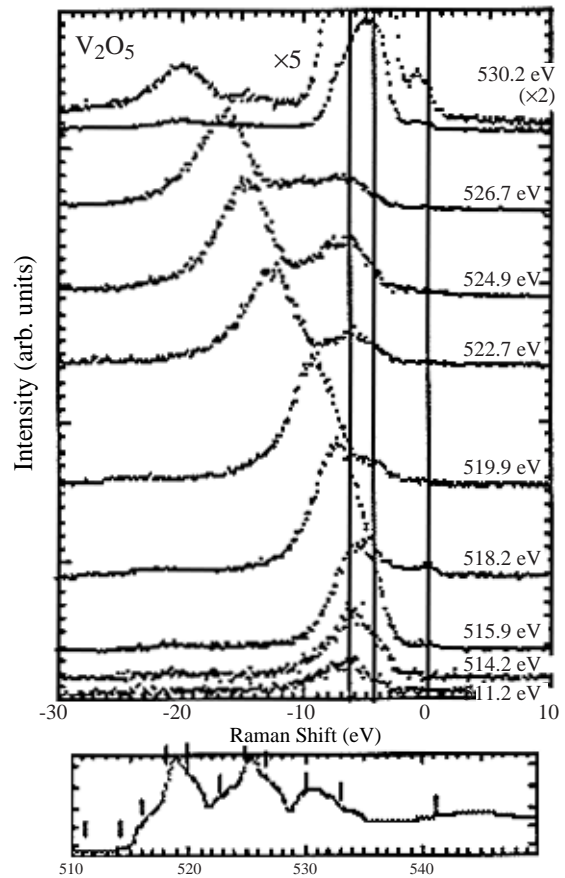


Fig. 3. Soft x-ray Raman spectra of V_2O_5 measured by various photon energies. The vertical bars correspond to the Raman scattering

Figure 4 shows the photoelectron spectrum and O1s absorption spectrum. Oxygen 1s absorption spectrum is used instead of the inverse photoemission spectrum, in order to know the conduction band. The 6.2 eV of the Raman band corresponds to the transition from the valence band to the conduction band peaks, as shown by the arrow in Fig.4. Such a similar assignment has been carried out in the SXES of TiO_2 .⁴

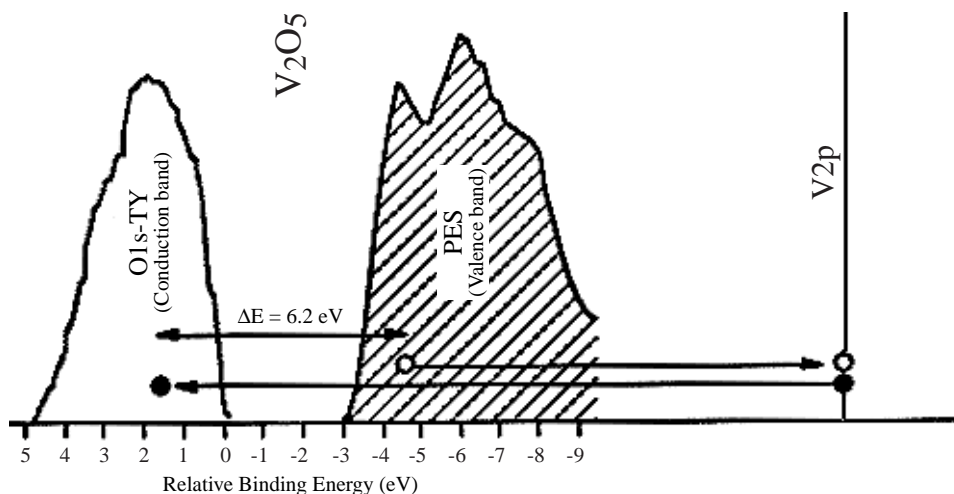


Fig. 4. Schematic diagram of soft x-ray Raman scattering of V_2O_5 by O1s total yield and photoemission spectra.

Another assignment of this Raman band might be the charge transfer transition when one consider the localized electron picture. Figure 5 shows the photoemission spectra of Sc, Ti, and V compounds in the valence band energy region.⁵ They have no 3d electrons nominally. These are the main valence bands which mainly consist of the ligand 2p components hybridized by 3d components. The features located below the main bands are the charge transfer satellite structures.

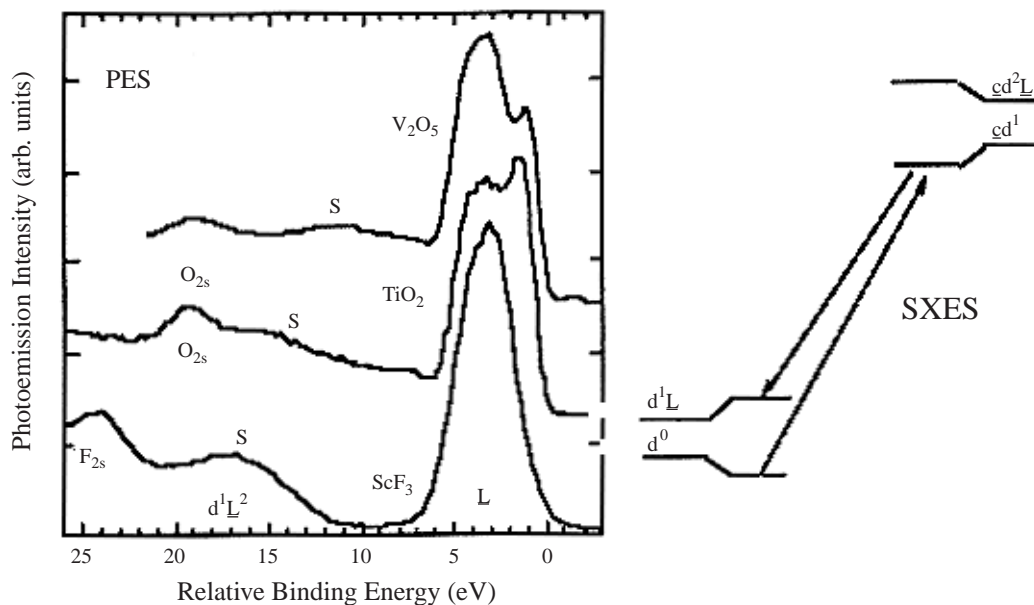


Fig. 5. Photoemission spectra of nominally d^0 system, V_2O_5 , TiO_2 , and ScF_3 . Right panel shows the schematic diagram of soft x-ray Raman scattering of nominally d^0 system by cluster picture.

The energy separation is mainly determined by the hybridization energy and the charge transfer energy. Clearly the intensity and the binding energy decrease from Sc to V compounds. This fact reflects the decreasing charge transfer energy. The right panel of the Fig.5 shows the schematic diagram of the Raman scattering, when it is considered by the localized electron picture of the cluster. In this case, the Raman scattering is assigned to be the transition to the charge transfer state $d^1\bar{L}$.

In the case of scandium compounds, it is better to consider the charge transfer transition, instead of the transition from valence band to conduction band. In the case of ScF_3 , there are two satellite structures of photoemission spectra.⁶ The satellite at about 13 eV is called as the bonding state and that at about 10 eV is called as nonbonding state. The photon energy dependence of the Sc2p soft x-ray emission spectra of ScF_3 shows that there are two groups in the Raman scattering. This Raman scattering does not change much by the excitation energy. These two Raman scattering well correspond to the two satellite structures which are seen in the photoemission spectra. When one considers the localized electron picture of the nominally d^0 system, the ground state is made by the hybridization between d^0 and the charge transfer state $d^1\bar{L}$. The hybridized states make three states including nonbonding state. Thus, we can see one Rayleigh scattering and two Raman scattering.

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